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(54) MANUFACTRE OF ELECTRODES FOR SECONDARY BATTERY, AND MANUFACTURE OF SECONDARY BATTERY

(57)Abstract:

PROBLEM TO BE SOLVED: To provide the manufacturing method of electrodes capable of providing batteries having an excellent cycle characteristic, besides the capacity, a rate characteristic and safety of the battery.

SOLUTION: This manufacturing method has a coating process for coating a conductive electrode base material with a coating including the active material and/or the conductive material, a binder and a solvent, and a drying process for drying the applied coating so as to form a coating film. In the case where the time to be required for drying till the solvent content in the applied coating becomes 10 wt.% in the drying process is expressed with T (sec), T is set so as to satisfy an inequality $45 \leq T \leq 1000$.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention relates to the rechargeable battery which used the electrode for rechargeable batteries, and it.

[0002]

[Description of the Prior Art] In recent years, the miniaturization of various devices, such as camcorder/movie equipment, audio equipment, a pocket mold computer, and a cellular phone, and lightweight-ization are progressing, and the high performance-ized request to the cell as a power source of these devices is increasing. Development of the lithium secondary battery which can realize the cycle property which are a high voltage and a high energy consistency as a cell of the source of power of an electric vehicle especially, and was excellent prospers. A lithium secondary battery consists of the positive electrode and negative electrode which usually come to form the electrode material layer containing an active material on conductive electrode substrates (charge collector), such as a metal, and an electrolyte layer formed among them.

[0003] In order to raise the safety of the nonaqueous electrolyte used for the lithium secondary battery in recent years, development of the polymer electrolyte to which the electrolytic solution was made to contain and carried out immobilizing is performed for example, to the gel polymer in nonaqueous electrolyte. Since the rechargeable battery using such a polymer electrolyte is lightweight and has configuration flexibility as compared with a liquid system, thin-film-izing like the shape of a sheet is possible for it, and it has the advantageous point that creation of a light weight and a space-saving cell is attained, for example.

[0004] Amelioration of an electrode material layer or a conductive electrode substrate is tried towards high-performance-izing of rechargeable batteries including such a lithium secondary battery. However, since an old electrode was not enough as the adhesive property of a conductive electrode substrate and an electrode material layer, a coat tended to exfoliate from a charge collector and there was a trouble that exfoliation of the electrode which the handling and processing on manufacture are not only very difficult, but runs gradually in the charge and discharge of a cell degraded a cycle property.

[0005] In the rechargeable battery which was going to attain especially thin film-ization, since the cell and structure which were enclosed with the conventional metallic conduit differ from each other greatly, the adhesive property of the conductive electrode substrate of an electrode and an electrode material coat poses a big problem. For example, when containing the monotonous laminating mold cell which carried out the laminating of the electrodes to plate-like in a flexible case and coming to close under a vacuum, in order not to start in the thickness direction of a cell in the prevention aggressiveness more than atmospheric pressure, the adhesive strength of the proper between an electrode material layer and a conductive electrode substrate poses a big problem.

[0006] About improvement in adhesive strength, add the ingredient which has the function which raises an adhesive property to an electrode material until now, a glue line (under coat etching primer layer) is prepared, or the attempt of improving the configuration and front-face nature of a conductive base

material is made. however -- that any approach has an inadequate adhesive property in having a bad influence on the electrode engine performance, or productivity being low **** -- as -- it was not what may satisfy all.

[0007]

[Problem(s) to be Solved by the Invention] This invention was made that the trouble in this conventional technique should be improved, the purpose can improve sharply the adhesive property between a conductive electrode substrate and an electrode material layer, and can raise the engine performance of the cell itself, such as a handling low price, yield, a cycle property, etc. on manufacture, and it is in offering the cell of high performance, and an efficient manufacture process as a result.

[0008]

[Means for Solving the Problem] this invention persons completed a header and this invention for that the desiccation process after applying the coating of an electrode material layer and the coating of an under coat etching primer layer (these layers may be summarized below and it may be called a "contact layer") on a conductive electrode substrate is important, and an adhesive property improving greatly by taking the long drying time in this desiccation process further, as a result of inquiring in order to attain the above-mentioned purpose.

[0009] Namely, the spreading process which applies the coating with which the summary of this invention contains an active material and/or the conductive matter, a binder, and a solvent on a conductive electrode substrate, It is T (sec) about the time amount which desiccation until the solvent content in the applied coating becomes 10% of the weight in said desiccation process in the manufacture approach of the electrode for rechargeable batteries of having the desiccation process which dries the applied coating and forms a paint film takes. It is [0010] when it carries out.

[Equation 6] $45 \leq T \leq 1000$ [0011] It consists in the manufacture approach of the electrode for rechargeable batteries characterized by carrying out. Moreover, other summaries of this invention are set to the manufacture approach of a rechargeable battery of having the cell element which consists of a positive-electrode layer, a negative-electrode layer, and an electrolyte layer. The spreading process at which either [at least] this positive-electrode layer or this negative-electrode layer applies the coating containing an active material and/or the conductive matter, a binder, and a solvent on a conductive electrode substrate, It is T (sec) about the time amount which desiccation until the solvent content in the coating which was formed through the desiccation process which dries the applied coating and forms a paint film, and was applied in said desiccation process becomes 10% of the weight takes. It is [0012] when it carries out.

[Equation 7] $45 \leq T \leq 1000$ [0013] It consists in the manufacture approach of the rechargeable battery characterized by carrying out.

[0014]

[Function] Generally, it is known that a desiccation process will consist of three processes of an ingredient pre-heating period, a constant drying period, and a falling-drying-rate period. if a solvent is a single component system in a constant drying period -- the amount w of content solvents Time amount t between -- $dw/dt =$ -- although the relation of being fixed is realized and surface desiccation of the film becomes rate-limiting, since liquid viscosity is rising, a falling-drying-rate period becomes rate-limiting [not a vapor rate but the diffusion rate in the film]. Although it is thought that the adhesive problem which it is mainly going to solve by this invention is based on generating of the internal stress of a paint film, it is thought that it depends for extent of this internal stress on this falling-drying-rate period.

[0015] However, according to examination of this invention persons, it is thought that not only the so-called decreasing drying process but the phase before that has done effect important for an adhesive property. That is, although an opening will be generated in a paint film by evaporation of the solvent in a paint film, if evaporation of a solvent is too intense, an opening will be generated also between a contact layer and a conductive electrode substrate, and it will be thought that a substantial touch area decreases.

[0016] In this invention, by having taken the time amount long enough which the amount of solvents in a coating reduces even to 10% of the weight with 45 seconds or more, when the amount of openings by evaporation of a solvent decreased, consequently the substantial touch area of a contact layer and a

conductive electrode substrate increased, it is thought that an adhesive property and adhesion improved. Since it can control that a binder deposits on a charge collector when the amount of solvents, on the other hand, makes time amount reduce even to 10% of the weight 1000 or less seconds, upright-ization of the electrode by the increment in the binder concentration in a conductive electrode substrate interface can be control as a result electronic conduction nature not only becomes good, but and flexibility can be secure, it is think that it is hard that it comes to generate the exfoliation and the curl by difference of stiffness with a conductive electrode substrate.

[0017]

[Embodiment of the Invention] Hereafter, although this invention is explained to a detail, it explains centering on the lithium secondary battery using the lithium secondary battery, especially the polymer electrolyte as a rechargeable battery made into the expedient upper object of explanation. About other cells, it is applicable by changing an ingredient suitably from the following publication.

[0018] In this invention, as a conductive electrode substrate, problems, such as elution, do not arise electrochemically but a metal and an alloy are usually used [using various kinds of things which may function as a charge collector of a cell] for ****. In the case of a lithium secondary battery, aluminum, copper, nickel, SUS, etc. can be mentioned as an example. Since the surface roughening process of the front face of these base materials is carried out beforehand and the binding effectiveness of a thing [Lycium chinense and] with a forward negative-electrode layer improves, it is a desirable approach. The mechanical grinding method which grinds a current collection body surface with the wire brush equipped with the approach of rolling out with blasting processing or a split-face roll, the coated abrasives which fixed the abrasive material particle, a grinding stone, an emery buff, steel wire, etc. as the surface surface roughening approach, electrolytic polishing, chemical polishing, etc. are mentioned.

[0019] Moreover, the weight of a rechargeable battery is reduced, namely, in order to raise a weight energy density, the hole vacancy type base material like an expanded metal or a punching metal can also be used. In this case, modification also of weight is attained free by changing that numerical aperture. Moreover, since the touch area of a paint film and a base material becomes small when a numerical aperture becomes too much high, although it was in the inclination for exfoliation of a paint film to stop being able to happen further easily due to the rivet effectiveness of the paint film which lets this hole pass when a contact layer is formed in both sides of a such punching type base material, bond strength may become low on the contrary.

[0020] The thickness of a conductive electrode substrate is 5 micrometers or more preferably, and is usually 50 or less preferably 100 micrometers or less 1 micrometers or more. When too thick, the capacity of the whole cell will fall too much, and handling may become difficult when too conversely thin. As an ingredient coating applied on a conductive electrode substrate, the electrode material coating containing an active material, a binder, and a solvent and the under coat etching primer ingredient coating containing a conductive ingredient, a binder, and a solvent are mentioned. When an under coat etching primer layer is prepared on a conductive electrode substrate, an electrode material layer is formed upwards at the pan of an under coat etching primer layer. An electrode material layer can be formed by drying after applying the electrode material coating containing an active material, a binder, and a solvent.

[0021] As an active material used for an electrode material coating, various kinds of ingredients which can be used for a positive electrode or a negative electrode can be used. As what can be used as positive active material of a lithium secondary battery, inorganic compounds, such as oxide of transition metals, such as Fe, Co, nickel, and Mn, a multiple oxide with a lithium, and a sulfide, are mentioned, for example. concrete -- MnO, V₂O₅, and V₆ -- O₁₃ and TiO₂ etc. -- transition-metals sulfide powder, such as multiple oxide powder of lithiums, such as transition-metals oxide powder, a nickel acid lithium, and a cobalt acid lithium, and transition metals, TiS₂, and FeS, is mentioned. Moreover, organic compounds, such as conductive polymers, such as for example, the poly aniline, can be mentioned as positive active material. Of course, two or more sorts of the above-mentioned active material may be mixed and used. 1-30 micrometers of particle size when an active material is granular are usually about 1-10 micrometers preferably at the point that cell properties, such as a rate property and a cycle

property, are excellent. As what can be used as a negative-electrode active material of a lithium secondary battery, it can consider as the compound which can occlusion emit Li ion other than Li metallic foil, and graphite, corks, etc. can be mentioned. The particle size of a granular negative-electrode active material is the point that cell properties, such as initial effectiveness, a rate property, and a cycle property, are excellent, and is usually about 15-30 micrometers preferably 1-50 micrometers.

[0022] Although there will be especially no limit to the electrolytic solution etc. as a binder used for an electrode material coating if stable, various kinds of ingredients are used from viewpoints, such as weatherability, chemical resistance, thermal resistance, and fire retardancy. Specifically Silicate, an inorganic compound like glass, and polyethylene, Alkane system polymers, such as polypropylene, Polly 1, and 1-dimethyl ethylene; Polybutadiene, Partial saturation system polymers, such as polyisoprene; Polystyrene, poly methyl styrene, The polymer which has rings, such as polyvinyl pyridine and Polly N-vinyl pyrrolidone; A polymethyl methacrylate, Polymethacrylic acid ethyl, polymethacrylic acid butyl, polymethylacrylate, Acrylic derivative system polymers, such as polyacrylic acid ethyl, polyacrylic acid, polymethacrylic acid, and polyacrylamide; Pori vinyl fluoride Fluororesin, such as polyvinylidene fluoride and polytetrafluoroethylene; A polyacrylonitrile, CN radical content polymers, such as the poly vinylidene cyanide; conductive polymers, such as halogen content polymer; poly anilines, such as polyvinyl alcohol system polymer; polyvinyl chlorides, such as polyvinyl acetate and polyvinyl alcohol, and a polyvinylidene chloride, etc. can be used. Moreover, it can be used even if it is mixture, such as the above-mentioned polymer, a conversion object, a derivative, a random copolymer, an alternating copolymer, a graft copolymer, a block copolymer, etc. the weight molecular weight of these resin -- usually -- 10000-3 million -- it is 100000 to about 1 million preferably. When too low, it is in the inclination for the reinforcement of a paint film to fall. On the other hand, when too high, viscosity may become high and formation of an electrode may become difficult. Desirable binder resin is fluororesin and CN radical content polymer.

[0023] The amount of the binder used to the active material 100 weight section is more than 1 weight section preferably, and is usually below 20 weight sections preferably below 30 weight sections more than the 0.1 weight section. When there are too few amounts of a binder, it is in the inclination for the reinforcement of an electrode to fall, and when there are too many amounts of a binder, it is in the inclination for ionic conductivity to fall. In order to raise the conductivity of an electrode, and a mechanical strength, the additive which discovers various kinds of functions, such as a conductive ingredient and reinforcing materials, fine particles, a filler, etc. may be made to contain in an electrode material coating. Although there will be especially no limit if optimum dose mixing is carried out and conductivity can be given to the above-mentioned active material as a conductive ingredient, carbon powder, such as acetylene black, carbon black, and a graphite, the fiber of various kinds of metals, a foil, etc. are usually mentioned. The DBP oil absorption of the carbon powder conductivity matter has desirable 120 cc / 100g or more, and especially its 150 cc / 100g or more are desirable from the reason for holding the electrolytic solution. As an additive, in order that trifluoro propylene carbonate, 1, 6-Dioxaspiro[4, 4] nonane-2, 7-dione, the 12-crown-4-ether, vinylene carbonate, catechol carbonate, etc. may raise the stability of a cell, and a life, it can be used. As reinforcing materials, inorganic [various kinds of], an organic globular shape, a fibrous filler, etc. can be used.

[0024] Although inorganic various kinds of [organic and] things can be used as a solvent used for an electrode material coating according to the active material and binder to be used, N-methyl pyrrolidone and dimethylformamide can be mentioned, for example. Although concentration of the solvent in a coating is made larger than at least 10 % of the weight, it is usually 35 % of the weight or more 20% of the weight or more more preferably [it is desirable and / size and a pan] than 30 weight. Moreover, as a minimum, they are usually 80 or less weight preferably 90 or less % of the weight. If too high, while spreading may become difficult when solvent concentration is too low, and it will become difficult to raise spreading thickness, the stability of a coating may get worse.

[0025] Generally the thickness of the paint film of the electrode material coating after a desiccation process is about 0.05 - 200 micrometers. Also in this range, it is 20 micrometers or more preferably, and 10 micrometers or more 200 micrometers or less are usually 150 micrometers or less preferably. When

too thin, it is not only hard coming to secure homogeneity, but spreading becomes difficult and the capacity of a cell may become small too much. On the other hand, when too thick, a rate property may fall too much.

[0026] An under coat etching primer layer can be prepared between an electrode layer and a conductive electrode substrate. When an under coat etching primer layer is prepared on a conductive electrode substrate, the function of an etching primer layer is raising the adhesive property of the electrode layer to a conductive electrode substrate, and can prevent reduction of the cell internal resistance by adhesive improvement, and the rapid capacity fall by the paint film desorption from the base material in a charge-and-discharge cycle trial process compared with the case where an etching primer layer is not prepared. An under coat etching primer layer can be made to form by drying this after applying the under coat etching primer ingredient coating containing a conductive ingredient, a binder, and a solvent on a conductive electrode substrate.

[0027] As a conductive ingredient used for an under coat primer layer, although carbon materials, such as carbon black and graphite, metal fine particles, conductive organic conjugated-system resin, etc. can be mentioned, it is the carbon black and graphite which may function also as an active material of an electrode layer preferably. The same thing as the binder and solvent which are used for said electrode material coating can be used for the binder used for an under coat primer layer, or a solvent. Moreover, since conductive resin, such as the poly aniline, polypyrrole, the poly acene, a disulfide system compound, and a polysulfide system compound, can have the function of both said conductive ingredients and binders, this can be used for an under coat primer layer to serve both as both conductive ingredient and binder.

[0028] When a conductive ingredient and a binder are used, respectively, the rate of a binder to a conductive ingredient is 5 % of the weight or more preferably, and is usually 100 or less % of the weight preferably 300 or less % of the weight 1% of the weight or more. If too low, the reinforcement of a paint film will fall and it will be easy to produce the exfoliation on a process etc. at the time of cell use. When too high, conductivity may fall and a cell property may fall.

[0029] moreover -- although solvent concentration in an under coat etching primer ingredient coating is usually made larger than at least 10 % of the weight -- desirable -- 20 % of the weight or more -- further -- desirable -- 30 weight -- size -- it is 35 % of the weight or more most preferably. Moreover, it is usually 80 or less % of the weight preferably 90 or less % of the weight. If too high, while spreading may become difficult when solvent concentration is too low, and it will become difficult to raise spreading thickness, the stability of a coating may get worse.

[0030] Although the thickness of the paint film of the under coat etching primer ingredient coating after a desiccation process will not be limited especially if an adhesive property and conductivity are secured, generally it is about 0.05 - 200 micrometers. Also in this range, it is 0.1 micrometers or more preferably, and 0.05 micrometers or more 10 micrometers or less are usually 1 micrometer or less preferably. If too thin, spreading will become difficult and it will be hard coming to secure homogeneity. When too thick, the volume capacity of a cell may fall too much.

[0031] An electrode material coating and an under coat etching primer ingredient coating can distribution-coating-ize each constituent with a ball mill, a sand mill, a 2 shaft kneading machine, etc., and can usually manufacture it. Although there will be especially no constraint if it is the range which can be treated with a coater and a liquid feed gear as viscosity range of a coating, from the ease of spreading, preferably, it is 1000cps or more still more preferably, and 100cps [100000cps or less] or more 1 million cps or less is usually 10cps or more usually 30000cps or less still more preferably.

[0032] Next, the method of applying for forming an under coat etching primer layer and/or an electrode layer on a conductive electrode substrate is indicated. Although it is not limited, especially concerning a coater but slide coating, die coating of an extrusion die, a reverse roll, gravure, a knife coating machine, a kiss coating machine, micro gravure, a knife coating machine, a rod coating machine, a blade coating machine, etc. are mentioned, an extrusion method is the most desirable when viscosity, spreading thickness, etc. of a coating are taken into consideration.

[0033] The coating (an electrode material coating and/or under coat etching primer ingredient coating)

applied on the conductive electrode substrate is T (sec) about the time amount which desiccation to 10 % of the weight takes to the solvent content in the applied coating by this invention although it subsequently dries. It is [0034] when it carries out.

[Equation 8] $45 \leq T \leq 1000$ [0035] It makes it indispensable to carry out. T is 60 or more most preferably 55 or more still more preferably 50 or more. Moreover, T is 200 or less 600 or less 900 or less preferably. If T is too large, a binder may deposit on a charge collector, electronic conduction nature may become poor a dryer not only becomes large beyond the need, but, and it will further become easy to produce exfoliation and curl between conductive electrode substrates. Moreover, when too small, it is in the inclination for the adhesive property and the adhesion of a conductive electrode substrate and a contact layer to get worse.

[0036] Moreover, it is possible to heighten the effectiveness of this invention further by dividing into the time amount t1 which takes time amount T for solvent content to become 30% of the weight, and the time amount t2 required by 10 % of the weight from 30 % of the weight, and making the above t1 and t2 into a predetermined value, respectively. That is, as t1, it is 30 or more most preferably 20 or more still more preferably ten or more, and is 120 or less most preferably 600 or less still more preferably 900 or less. Moreover, it is 120 or less most preferably 300 or less still more preferably 400 or less still still more preferably more preferably [are 20 or more still more preferably ten or more preferably as t2, and are 900 or less preferably, and / 600 or less]. In addition, in case t1 and t2 are made into the above-mentioned value, respectively, it is necessary to make larger than 30 % of the weight average solvent content in the coating with which spreading is presented.

[0037] Furthermore, if time amount t3 (sec) taken for the amount of solvents in a coating to become 0.1% of the weight from 10 % of the weight is made especially into 3 seconds or more and 10 more seconds or more 1 second or more, since the adhesive property of a contact layer and a conductive electrode substrate can be raised further, it is desirable. Since a dryer not only becoming large beyond the need but a binder may deposit on a charge collector on the other hand if t3 is too large, electronic conduction nature may become poor and it further becomes easy to produce exfoliation and curl between conductive electrode substrates, t3 (second) is [500 or less] usually desirable, and it is 30 or less most preferably 60 or less still more preferably 120 or less.

[0038] Although the method directly heated from a rear face as the desiccation approach with the method which circulates hot blast, the method which gives the radiant heat, a heating roller, etc. can be used, it is the method which circulates hot blast preferably in respect of simplicity. As the control approach of T, t1, t2, and t3, there is the approach of controlling the temperature of hot blast, circulation velocity, the blasting distance to a paint film, an include angle, etc. by the method which circulates hot blast. Moreover, in desiccation by the radiant heat, such as infrared radiation, it is controllable by infrared reinforcement, wavelength, etc. Moreover, it is controllable also by controlling the die length of a desiccation zone, and the feed rate of a paint film, and changing the residence time in the desiccation zone of a paint film. In this, the die length of a desiccation zone may have the constraint on equipment. The feed rate of a paint film can be preferably used as a controlling factor in the range from which productivity does not fall. In respect of simplicity, the value of T, t1, t2, and t3 which are made into the purpose by adopting the method which circulates hot blast and controlling the temperature of hot blast, circulation velocity, etc. is attained preferably. What is necessary is to be the interior of a series of dryers, and just to set up the whole desiccation conditions as control according to individual of t1 and t2, so that the predetermined range may be attained. Since the approach of dividing into a zone which is different, using especially a dryer two or more sets can set up temperature, circulation velocity, etc. which are different by each, it is easy to control and they is desirable. The drying temperature generally used in this invention is 70 degrees C or more preferably, and is usually 140 degrees C or less preferably 180 degrees C or less 40 degrees C or more.

[0039] When an under coat etching primer layer is first formed on a conductive electrode substrate, an electrode material layer will be formed on it. In this case, although the formation approach of an electrode material layer and its presentation can be performed like above-mentioned technique, even if out of range, the adhesive property with an under coat etching primer layer is fully securable [it is not

necessary to necessarily adhere to the aforementioned approach and instantiation, this invention prescribes especially desiccation conditions, and].

[0040] as the formation approach of these layers, when forming an under coat etching primer layer and an electrode material layer, after applying and drying an under coat etching primer ingredient coating on a conductive electrode substrate, the so-called wet-on-dry spreading which applies an electrode material coating may be carried out, and an electrode material coating is applied on the under coat etching primer layer of a damp or wet condition -- being the so-called -- wet-on-wet spreading can also be carried out. In the case of the wet-on-wet applying method, the wet-on-wet multilayer coincidence applying method which applies each class to coincidence may be adopted. Moreover, by collecting after [all] layer spreading in any case, and performing back process processing of desiccation, heat curing, etc., although the wet-on-wet serial applying method for recoating each class one by one in liquefied voice may be adopted The adhesive property between a base material and an under coat primer layer and between an under coat etching primer layer and an electrode layer can be raised further. Thereby, dispersion in internal impedance and the cell engine performance about charge and discharge can be reduced sharply, and the performance degradation by the repeat of charge and discharge can also be reduced. As a coater which can be used in wet-on-wet multilayer coincidence spreading, although slide coating, die coating of an extrusion die, etc. are mentioned, when coating viscosity, spreading thickness, etc. are taken into consideration, an extrusion method is desirable. moreover, wet-on-wet -- independent [in spreading methods much more more various than multilayer simultaneous methods other than an extrusion die method, such as a reverse roll, gravure, a knife coating machine, a kiss coating machine, micro gravure, a knife coating machine, a rod coating machine, and a blade coating machine,] as a coater which can be used serially in spreading -- or it can combine and adopt. Moreover, it is also possible to carry out imprint lamination spreading of another layer of a damp or wet condition [finishing / spreading to another base material] depending on a lower layer damp or wet condition or viscosity, and to consider as the upper layer.

[0041] In the wet-on-wet multilayer coincidence applying method or the wet-on-wet multilayer serial applying method, the ratio of the viscosity of an under coat primer ingredient coating and an electrode material coating can usually perform multilayer spreading easily 1:100-100:1 and by taking 1:10 about for -10:1 preferably. It is T (sec) about the time amount which desiccation to 10 % of the weight takes to the applied average solvent content of an under coat etching primer ingredient coating and the whole electrode material coating in this invention when applying serially the under coat etching primer ingredient coating and electrode material coating like the wet-on-wet multilayer coincidence applying method or the wet-on-wet multilayer serial applying method on a conductive electrode substrate in coincidence or this order, while both have been damp or wet conditions. It is [0042] when it carries out. [Equation 9] $45 \leq T \leq 1000$ [0043] It carries out. About desirable T, t1, t2, and t3, it is the same as that of the above. Next, an electrolyte and an electrolyte layer are explained. the electrolytic solution which consists of a supporting electrolyte (solute) and a solvent as an electrolyte layer formed between a positive electrode and a negative electrode, and the polymer electrolyte which held this by the polymer - various kinds of electrolytes, such as a perfect solid-state mold electrolyte, can be used further.

[0044] In the case of a lithium secondary battery, it is common to use what dissolved the electrolyte which is lithium salt in the non-aqueous solvent as the electrolytic solution. as the lithium salt as a supporting electrolyte -- LiPF6, LiAsF6, LiSbF6, LiBF4, LiClO4, LiI, LiBr, LiCl, LiAlCl, LiHF2, LiSCN, and LiSO3 CF2 etc. -- it can mention. Especially among these, it is LiPF6. And LiClO4 It is suitable. Generally the content in the electrolytic solution of these supporting electrolytes is 0.5 - 2.5 mol/L.

[0045] Although especially the class of solvent used for the electrolytic solution is not limited, the solvent of comparatively a high dielectric constant is used suitably. Specifically, one sort or two sorts or more of mixture, such as nitril, such as sulfur compounds, such as lactone, such as glymes, such as un-annular carbonate, such as annular carbonate, such as ethylene carbonate and propylene carbonate, dimethyl carbonate, diethyl carbonate, and ethyl methyl carbonate, a tetrahydrofuran, 2-methyl tetrahydrofuran, and dimethoxyethane, and gamma-butyl lactone, and sulfolane, and an acetonitrile, can

be mentioned. Especially among these, one sort or two sorts or more of mixed solutions chosen from unannular carbonate, such as annular carbonate, such as ethylene carbonate and propylene carbonate, dimethyl carbonate, diethyl carbonate, and ethyl methyl carbonate, are suitable.

[0046] When using a polymer electrolyte, it considers as gel by holding the above-mentioned electrolytic solution by the polymer. Although the concentration to the electrolytic solution of a polymer is based also on the molecular weight of the polymer to be used, it is usually 0.1 to 30 % of the weight. When concentration is too low, it may be hard coming to form gel, the holdout of the electrolytic solution may fall, and the problem of a flow and a liquid spill may arise. Moreover, if concentration is too high, while viscosity will become high too much and will produce process top difficulty, it is in the inclination for the rate of the electrolytic solution to fall, for ionic conductivity to fall, and for cell properties, such as a rate property, to fall.

[0047] As an approach of forming a polymer electrolyte, the above-mentioned electrolytic solution Polyethylene oxide, Although it can obtain by dipping in polymers, such as isocyanate bridge formation objects, such as polypropylene oxide and polyethylene oxide, phenylene oxide, and a phenylene sulfide system polymer, etc. The approach (1) of performing polymerization, such as ultraviolet curing and heat curing, for the polymerization nature monomer content electrolytic solution, and the approach (2) of cooling what carried out the elevated-temperature dissolution of the macromolecule which forms a gel electrolyte in ordinary temperature into the electrolytic solution are used preferably.

[0048] In the case of the former approach (1) using the polymerization nature monomer content electrolytic solution, as a polymerization nature monomer, what has partial saturation double bonds, such as an acryloyl radical, a methacryloyl radical, a vinyl group, and an allyl group, for example is raised. Specifically An acrylic acid, a methyl acrylate, an ethyl acrylate, ethoxyethyl acrylate, Methoxy ethyl acrylate, ethoxyethoxyethyl acrylate, Polyethylene-glycol monoacrylate, ethoxyethyl methacrylate, Methoxy ethyl methacrylate, ethoxyethoxyethyl methacrylate, Polyethylene glycol monomethacrylate, N, N diethylamino ethyl acrylate, N, N dimethylamino ethyl acrylate, glycidyl acrylate, Allyl compound acrylate, acrylonitrile, N-vinyl pyrrolidone, diethylene glycol diacrylate, Triethylene glycol diacrylate, tetraethylene glycol diacrylate, Polyethylene-glycol diacrylate, diethylene-glycol dimethacrylate, Triethylene glycol dimethacrylate, tetraethylene glycol dimethacrylate, Polyethylene glycol dimethacrylate, polyalkylene glycol diacrylate, Polyalkylene glycol dimethacrylate etc. can be used. Further Trimethylol propane alkoxy RETOTORI acrylate, Monomers of four or more organic functions, such as 3 organic-functions monomers, such as pentaerythritol alkoxy RETOTORI acrylate, pentaerythritol alkoxylate tetraacrylate, and ditrimethylol propane alkoxylate tetraacrylate, etc. can be used.

[0049] Since a reaction is effectively advanced in case the polymerization of these monomers is carried out with heat, ultraviolet rays, an electron ray, etc., a polymerization initiator can also be put into the electrolytic solution. As a polymerization initiator, a benzoin, benzyl, an acetophenone, a benzophenone, The id etc. can be used. a Michler's ketone, a biacetyl, and benzoyl PAO -- affected -- Furthermore, t-butylperoxyneodecanoate, alpha-cumil peroxy neodecanoate, t-hexyl peroxy neodecanoate, 1-cyclohexyl 1-methylethyl peroxy neo decanoate, Peroxy neo decanoate, such as t-amyl peroxy neo decanoate t-butyl peroxy neoheptanoate, alpha-cumyl peroxy neoheptanoate, Peroxy neoheptanoate, such as t-hexyl peroxy neoheptanoate, 1-cyclohexyl 1-methylethyl peroxy neoheptanoate, and t-amyl peroxy heptanoate, can be used.

[0050] By forming gel to the electrolytic solution as such a macromolecule in the case of the approach (2) of the latter which cools what, on the other hand, carried out the elevated-temperature dissolution of the macromolecule which forms a gel electrolyte in ordinary temperature into the electrolytic solution, although it can be used no matter it may be what thing, if stable as a cell ingredient For example, the polymer which has rings, such as polyvinyl pyridine and Polly N-vinyl pyrrolidone; A polymethyl methacrylate, Polymethacrylic acid ethyl, polymethacrylic acid butyl, polymethylacrylate, Acrylic derivative system polymers, such as polyacrylic acid ethyl, polyacrylic acid, and polymethacrylic acid polyacrylamide; Pori vinyl fluoride Fluororesin, such as polyvinylidene fluoride; CN radical content polymer; polyvinyl acetate, such as a polyacrylonitrile and the poly vinylidene cyanide, Polyvinyl

alcohol system polymers, such as polyvinyl alcohol; halogen content polymers, such as a polyvinyl chloride and a polyvinylidene chloride, etc. are mentioned. Moreover, it can be used even if it is the mixture of the above-mentioned macromolecule etc., a conversion object, a derivative, a random copolymer, an alternating copolymer, a graft copolymer, a block copolymer, etc. The range of the weight average molecular weight of these macromolecules is usually 10000-5 million. If molecular weight is low, it will be hard coming to form gel. If molecular weight is high, viscosity will become high too much and handling will become difficult.

[0051] Furthermore, it is also possible to use the electrolyte of the perfect solid-state mold formed with the macromolecule and the supporting electrolyte without using a solvent. It sinks into porous film, such as porous polyethylene, preferably, and an electrolyte is used as an electrolyte layer. Moreover, it can also be made to exist in a positive electrode and/or a negative electrode. When making a polymer electrolyte exist in a positive electrode and/or a negative electrode, you may differ, even if the polymer for holding said binder and said electrolytic solution is the same.

[0052] After applying the fluid coating which is a polymer electrolyte precursor on a positive electrode and/or a negative electrode as the desirable manufacture approach of the cell which used the polymer electrolyte and making it sink into the opening of an electrode, the approach of processing to a precursor and using as a polymer electrolyte is mentioned. In this case, it is still more desirable to make the polymer electrolyte of a positive electrode and/or a negative electrode and the polymer electrolyte layer of an electrolyte layer form in coincidence in one at the point which raises the safety of a cell and raises cell properties, such as a rate property. In the above in addition, as a polymer electrolyte precursor In said method (1) of performing polymerization, such as ultraviolet curing and heat curing, for the polymerization nature monomer content electrolytic solution The polymerization nature monomer content electrolytic solution can be used, and the solution which carried out the elevated-temperature dissolution of the macromolecule into the electrolytic solution can be used in said approach (2) of cooling what carried out the elevated-temperature dissolution of the macromolecule which forms a gel electrolyte in ordinary temperature into the electrolytic solution.

[0053] Since applying to the lithium secondary battery which has a non-fluidity electrolyte like a polymer electrolyte or a perfect solid-state mold electrolyte has the remarkable effect of the invention, the manufacture approach of this invention has it. [desirable] Although a cell element comes to carry out the laminating of a positive electrode and the negative electrode through an electrolyte layer, the effectiveness of this invention is large and it is desirable that the laminating of these is carried out to plate-like in this case. Because, since it is difficult for the direction of a laminating to make pressure act in the case of such a plate-like layer built cell, it is because the essential adhesive property of a conductive electrode substrate and a contact layer and adhesion are especially important.

[0054] Moreover, it is desirable for below atmospheric pressure to press down a cell element to the thickness direction at the point that the effectiveness of this invention is remarkable, and to be held by **. Such when [weak] it stops and is held by **, it is because the essential adhesive property of a conductive electrode substrate and a contact layer and adhesion are especially important like the above. Such a cell can manufacture a cell element by carrying out vacuum enclosure in the case which consists of a film which has flexibility.

[0055] After two or more laminatings of the cell element are carried out if needed, it is usually contained by the case. For example, in the case of the cell using a polymer electrolyte or a perfect solid-state mold electrolyte, a thin cell is realizable for the case which consists of a film which has flexibility like a lightweight and thin laminate film by carrying out vacuum enclosure. The film which consists of a metallic foil and a lamination material of a high polymer film as a laminate film can use it suitably. Of course, after enclosing a cell with a case, if required, it is also possible, since facilities, such as wearing to the device of a cell, are given to contain two or more cases in a sheathing case with rigidity.

[0056]

[Example] Hereafter, although this invention is further explained to a detail based on an example, this invention is not limited at all by the following example, in the range which does not change the summary, can be changed suitably and can be carried out.

[Preparation of a positive-electrode ingredient coating]

[0057]

[Table 1]

Presentation Cobalt acid lithium 92.0wt% Acetylene black 4.0wt% Polyvinylidene fluoride 4.0wt% N-methyl-2-pyrrolidone 67.0wt% [0058] The raw material mixture of the above-mentioned presentation was kneaded with the kneading machine for 2 hours, and it considered as the positive-electrode ingredient coating.

[Preparation of a negative-electrode ingredient coating]

[0059]

[Table 2]

Presentation Corks 92.0wt% Polyvinylidene fluoride 8.0wt% N-methyl-2-pyrrolidone 67.0wt% [0060] Like the positive electrode, the raw material mixture of the above-mentioned presentation was kneaded with the kneading machine for 2 hours, and it considered as the negative-electrode ingredient coating.

[Preparation of a polymer electrolyte precursor]

[0061]

[Table 3]

Presentation Tetra-ethylene glucohol diacrylate 20.0wt(s)% Polyethylene oxide 2.0wt(s)% Lithium perchlorate 15.0wt(s)% Polymerization initiator (Akuzo Nobel shrine Trignox 42) 0.5wt% Electrolytic solution (propylene carbonate) 100.0wt% [0062] It was presupposed that the mixed stirring dissolution of the mixture of the above-mentioned presentation was carried out, and it considered as the monomer content electrolytic solution.

[Preparation of an under coat etching primer ingredient]

[0063]

[Table 4]

Presentation Acetylene black 50.0wt% Polyvinylidene fluoride 50.0wt% N-methyl-2-pyrrolidone 900.0wt% [0064] The raw material mixture of the above-mentioned presentation was distributed in the disperser, and it considered as preparation of an under coat etching primer ingredient.

[0065] On the conductive electrode substrate which consists of aluminum with an example 1 thickness of 15 micrometers, said positive-electrode ingredient coating was applied so that the thickness after desiccation might be set to 100 micrometers with an extrusion-die die spreading method, and this was dried at 80 to 120 degree C with the method which circulates hot blast. Moreover, similarly, on the conductive electrode substrate which consists of copper with a thickness of 10 micrometers, said negative-electrode ingredient coating was applied so that the thickness after desiccation might be set to 100 micrometers with an extrusion-die die spreading method, and this was dried at 80 to 120 degree C with the method which circulates hot blast. Under the present circumstances, a positive electrode and a negative electrode adjust the temperature and airflow of a desiccation zone, and it was made to be set to $t_1=30$, $t_2=30$ and $t_3=60$. In addition, aluminum foil is put on each [which was dried according to predetermined desiccation conditions] paint film at the time, the quick stop of the evaporation of a solvent is carried out, and measurement of the solvent concentration in a desiccation process is 2 300cm of this electrode surface product. It asked by measuring and calculating the neighboring amount of residual solvents.

[0066] By the roll press of linear pressure 300 kgf/cm, consolidation of the obtained paint film was carried out, and it was used as the electrode. The adhesive property of the obtained electrode was evaluated as follows. On the other hand, said monomer content electrolytic solution was applied to this electrode layer, and it considered as the cell element by carrying out laminating postpolymerization plate-like. The cell element was used as the lithium secondary battery of a monotonous mold by carrying out a vacuum seal to the case which consists of a laminate film, and containing. The cycle property of the obtained cell was evaluated.

[0067] The **** break was put into the cutter to horizontal to the electrode sheet after a [adhesive strength evaluation] roll press at intervals of 1mm, and a perpendicular direction, and the grid of 1cm angle (100 pieces) was made. Under the present circumstances, only a paint film is cut and it was made

not to cut the conductive electrode substrate itself. Then, the cellophane tape was stuck by pressure so that all these grids might be started, the tape was removed, and the number of paint film grids which remained in the sample side was counted. A result is shown in Table -1.

[0068] [Cycle characterization] The discharge capacity maintenance factor after repeating charge and discharge about 20 obtained cell samples is 80% of the first stage. The number which it is above was counted. A result is shown in Table -2.

[0069] Except having changed the amount of example 2 hot blast and having been referred to as $t_1=60$ and $t_2=60$, like the example 1, the electrode and the cell were produced and the adhesive property and the cycle property were evaluated. A result is shown in Table -1 and -2.

[0070] On the conductive electrode substrate which consists of aluminum with an example 3 thickness of 15 micrometers, said under coat etching primer ingredient coating and said positive-electrode ingredient coating were applied at this order by the wet-on-wet coincidence applying method by the extrusion-die die spreading method. It was made, as for spreading thickness, for 1 micrometer and an electrode layer to be set to 100 micrometers by the under coat etching primer layer. Subsequently, this was dried at 80 to 120 degree C with the method which circulates hot blast. Moreover, said under coat etching primer ingredient coating and said negative-electrode ingredient coating were similarly applied at this order on the conductive electrode substrate which consists of copper with a thickness of 10 micrometers by the wet-on-wet coincidence applying method by the extrusion-die die spreading method. It was made, as for spreading thickness, for 1 micrometer and an electrode layer to be set to 100 micrometers by the under coat etching primer layer. Under the present circumstances, a positive electrode and a negative electrode adjust the temperature and airflow of a desiccation zone, and it was made to be set to $t_1=30$ and $t_2=30$. Like the example 1, the following produced the electrode and the cell and evaluated the adhesive property and the cycle property. A result is shown in Table -1 and -2.

[0071] Except having changed the amount of example of comparison 1 hot blast, and having been referred to as $t_1=20$ and $t_2=20$, like the example 1, the electrode and the cell were produced and the adhesive property and the cycle property were evaluated. A result is shown in Table -1 and -2.

[0072] Except having changed the amount of example of comparison 2 hot blast, and having been referred to as $t_1=35$ and $t_2=5$, like the example 1, the electrode and the cell were produced and the adhesive property and the cycle property were evaluated. A result is shown in Table -1 and -2.

[0073] Except having changed the amount of example of comparison 3 hot blast, and having been referred to as $t_1=20$ and $t_2=20$, like the example 3, the electrode and the cell were produced and the adhesive property and the cycle property were evaluated. A result is shown in Table -1 and -2.

[0074]

[Table 5]

表-1

	テープ剥離試験後の残存升目数 (正極及び負極の平均値)
実施例1	95
実施例2	98
実施例3	100
比較例1	54
比較例2	35
比較例3	65

[0075]
[Table 6]

表-2

	サイクル試験後の80%放電容量維持電池個数				
	充放電サイクル回数				
	5回	10回	50回	100回	200回
実施例1	20	20	20	18	17
実施例2	20	20	20	19	18
実施例3	20	20	20	20	20
比較例1	19	17	10	8	6
比較例2	15	10	5	2	0
比較例3	20	19	15	10	9

[0076]

[Effect of the Invention] According to this invention, it becomes possible to raise sharply the adhesive property over the base material of a paint film. Moreover, it not only can raise the capacity of a cell, a rate property, and safety, but it can raise a cycle property greatly. Moreover, since what is necessary is just to control desiccation conditions by this invention by making the amount of residual solvents into an index on production, it is size the place which contributes about both the production process

management side and engine-performance side of a cell. Moreover, there is also an advantage from which production condition optimization and process planning become easy.

[Translation done.]